Hydrolysis of cellulose to glucose by solid acid catalysts

Yao-Bing Huang and Yao Fu*

As the main component of lignocelluloses, cellulose is a biopolymer consisting of many glucose units connected through β-1,4-glycosidic bonds. Breakage of the β-1,4-glycosidic bonds by acids leads to the hydrolysis of cellulose polymers, resulting in the sugar molecule glucose or oligosaccharides. Mineral acids, such as HCl and H2SO4, have been used in the hydrolysis of cellulose. However, they suffer from problems of product separation, reactor corrosion, poor catalyst recyclability and the need for treatment of waste effluent. The use of heterogeneous solid acids can solve some of these problems through the ease of product separation and good catalyst recyclability. This review summarizes recent advances in the hydrolysis of cellulose by different types of solid acids, such as sulfonated carbonaceous based acids, polymer based acids and magnetic solid acids. The acid strength, acid site density, adsorption of the substance and micropores of the solid material are all key factors for effective hydrolysis processes. Methods used to promote reaction efficiency such as the pretreatment of cellulose to reduce its crystallinity and the use of ionic liquids or microwave irradiation to improve the reaction rate are also discussed.

1. Introduction

The discovery and utilization of fossil resources has changed the energy supplement of the whole world. Current energy systems are mainly based on these fossil resources such as coal, petroleum and natural gas. However, the rapid consumption of these resources, together with the resulting global warming caused by CO2 emissions, raises sustainability issues regarding the existing energy systems based on fossil resources. To solve this problem, people are forced to explore renewable resources to substitute the fossil resources in order to meet increasing energy demands.1-4 Until now, various forms of energy systems have been developed as excellent alternatives such as solar, wind, biomass, hydroelectric and geothermal.5,6 Among these new forms of energy sources, biomass is the only sustainable source of organic carbon on Earth, which is considered as one part of the solution for producing fuels and chemicals.7-9 Biomass can be obtained all over the world and it generally occurs in the form of organic materials such as grass, wood, agricultural crops and their residues and waste. These

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materials come from biological photosynthesis from CO₂, water and sunlight, thus making them sustainable and green feedstocks with zero carbon emission. The first generation of biofuels are mainly bioethanol and biodiesel which are produced from sugars, starches and vegetable oils. However, concerns were raised that the utilization of these materials competed with food for feedstocks. Moreover, their potential availability is limited by the amount of fertile soil.

Due to the above limitations, the second generation of biofuels has mainly concentrated on the utilization of lignocellulosic biomass. Lignocellulose can be grown in combination with food or on barren land. Every year, sees the formation of about 220 billion dry tons of available biomass (ca. 45 EJ of energy content), and lignocellulose forms about 70–95% of it. Lignocelluloses are composed of mainly three components, cellulose (40–50%), hemicelluloses (25–35%) and lignin (15–20%) (percentages of the components vary from different biomass resources). A schematic biorefinery for the utilization of lignocellulose is shown in Scheme 1. Among these biopolymers, cellulose is the most valuable one which can be converted into glucose and subsequently fermented into bioethanol or dehydrated into platform molecules. Besides, cellulosic biofuels have been considered as the most promising candidates for the replacement of current petroleum based fuels.

The first step for cellulose utilization is to depolymerize it into soluble oligosaccharides and glucose. However, the natural polymer forms a robust crystal structure with high chemical stability, thus making the depolymerization processes more difficult. The established methods for cellulose hydrolysis are known to be catalyzed by cellulose enzymes. But limitations of the enzymes systems are obvious in that the processes are always low efficiency and have a high enzyme cost. At the same time, much work has been concentrated on the hydrolysis of cellulose to glucose with mineral acids. Sulfuric acid is known as a typical acid for this reaction. However, the large-scale use of acid suffers from several problems such as reactor corrosion, catalyst recovery and requires treatment of the acid residue, producing lots of waste. From the industrial point of view, the above limitations must be taken into account when designing production processes. In addition, several aspects also need to be of concern such as economy, simplicity, efficiency and environmental friendliness.

The utilization of heterogeneous acids has the potential to overcome some of the above limitations due to the ease of separation of catalysts. Significant development of this transformation has been made by using various types of catalysts with large pore size and strong acid strength. Association with these solid acids, many pretreatment technologies have also been developed to reduce the crystallinity of cellulose and increase its surface area in order to improve the reaction efficiency and selectivity, for example, ball-milling, solubilization/precipitation in ionic liquids, liquid acids/alkaline solutions, the non-thermal atmospheric plasma method and so on. It is worth noting that most hydrolysis processes with solid acids require the pretreatment of cellulose as shown in Table 1. Apart from that, microwave irradiation induced assistance of the hydrolysis of cellulose is an effective heating method compared to conventional oil heating.

In this review, we summarize the recent advances in the hydrolysis of cellulose into glucose with solid acids. The review is divided into the following parts: (1) structure of cellulose; (2) hydrolysis of cellulose by liquid acids; (3) hydrolysis of cellulose by solid acids. The final part of this review presents an outlook of the future of this domain.

2. Structure of cellulose

Early exploration work on the structure of cellulose was carried out by Anseleme Payen. He obtained a resistant fibrous solid material with the formula C₆H₁₀O₅ after the treatment of various plant tissues with acids and ammonia. It was the

![Scheme 1](https://example.com/scheme1.png)

Scheme 1 Utilization of lignocelluloses to produce chemicals and fuels.
earliest “cellulose”.39 The structure of cellulose was elucidated in 1920 by Hermann Staudinger.40 He found that cellulose was composed of β-glucose units, linked to each other to form long chains (Scheme 2). The structure of cellulose was made up of many glucose moieties linked in the form of β-1,4-glycosidic units (AGUs). The AGUs are linked to each other through glycosidic bridges on the C1 and C4 carbon atoms.31

The number of repeating AGUs is defined as the degree of polymerization (DP) of cellulose. Generally, the DP of cellulose varies according to the original type of materials, for example, the common range of DP for wood pulp is about 300–1700 and is 800–10 000 for cotton or other plant fibers.41 Due to the huge number of hydroxyl groups and linkage of β-1,4-glycosidic bonds, it is easy to form intra- and intermolecular hydrogen bonds which make the cellulose resistant during chemical and biological treatment and make it highly insoluble in common solvents.42

According to the crystal features, cellulose has at least seven forms, Iα, Iβ, II, IIIα, IIIβ, IVα, IVβ.43,44 In nature, most cellulose occur in the state of Iα, Iβ. They can be found in the same material from almost every biomass source. The ratio of the two crystalline forms depends on the source of cellulose. Generally, cellulose Iα is rich in the cell walls of algae and bacterial cellulose while cellulose Iβ is abundant in cotton, wood and tunicate cellulose.45 Cellulose Iα,β is thermodynamically not the most stable form in nature.46 When cellulose I swells in concentrated sodium hydroxide, it easily forms the thermodynamically more stable cellulose II after the removal of the swelling agent.42,43 Cellulose III can be obtained by treatment of cellulose Iα, Iβ with the ammonia fiber explosion process. Cellulose IV can be obtained by treating cellulose III with glycerol at 206 °C.42,43 However, cellulose III, IV are not common and are thus ignored in our discussion. The more generally known and discussed forms of cellulose are microcrystalline Avicel cellulose and α-cellulose which come from pure bacterial cellulose and the treatment of wood with alkali extraction.47

3. Hydrolysis of cellulose by liquid acids

The hydrolysis of cellulose is a process to break the β-1,4-glycosidic bonds of the polymer which is an essential step for the conversion of cellulose and opens the possibility of subsequent catalytic transformations. Direct hydrolysis of lignocellulosic biomass with acids goes back to the early 19th century

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and several processes were reported to be effective in the 20th century. The first technology for the acid hydrolysis of cellulose was developed by Faith in 1923. In the process, sulfuric acid solution (0.5 wt%) was used to treat wood waste in bricklined percolators. After about 45 min at 170 °C, a dilute sugar solution was obtained. The solution was transferred for fermentation after neutralization. A 50% yield of sugars was obtained according to the theoretical yield of fermentable sugars.

After the work, many processes were reported to be effective in the hydrolysis of cellulose. They used different kinds of acids such as HCl, H2SO4, HF and organic acids (oxalic, maleic, furmaric). In 1937, Bergius reported the hydrolysis of cellulose with 40 wt% HCl (ca. 12 mol L−1) at room temperature. Cellulose was solubilized in concentrated acid together with hemicelluloses, leaving insoluble lignin. The hydrolysis products were glucose and oligosaccharides without dehydration products. Concentrated HCl (6–7 mol L−1) was also effective in the hydrolysis of cellulose in the presence of CaCl2 and LiCl as the additives. The results showed that the salts had a swelling effect by increasing the hydrolysis rate, leading to an 85% yield of glucose at 90 °C. Additionally, concentrated acids had an apparent swelling effect on cellulose. Cellulose swells when the sulfuric acid concentration is above 50%. Camacho et al. studied the effect of H2SO4 concentration (from 31%–70%, w/v) on the solubilization rate of microcrystalline cellulose, revealing that acid promoted the total solubilization of cellulose when the concentration was above 62%. Although hydrolysis with concentrated acids operates at low temperature and atmospheric pressure, these processes had strict requirements on water content and displayed severe corrosion.

Hydrolysis of cellulose with dilute acid usually requires high temperature. Madison et al. reported a treating process in which wood was treated with 0.5 wt% H2SO4 in a continuous reaction. The degradation of products was minimized for the short residence time of cellulose in the reactor. Another successful process using an isothermal plug flow reactor was reported by Grethlein and Thompson. They used 1 wt% H2SO4 in the continuous process at 240 °C with a short residence time of 0.22 min; 50% glucose was obtained at last. A few years later, Harris et al. used a two stage system containing dilute H2SO4 in the saccharification of wood. After the hemicellulose was extracted, cellulose was transferred for hydrolysis and a high purity of glucose was obtained.

The hydrolysis of cellulose was achieved with gaseous HCl as reported by the Wilke group. The HCl stream was adsorbed on the dried wood particles and initiated the hydrolysis of hemicelluloses. After extraction of the hemicellulose sugars, the residue was dried and mixed with HCl gas at 45 °C, achieving 90% conversion of the available carbohydrate content of wood to sugars. High pressure HCl systems were also reported for the hydrolysis reaction. Apart from gaseous HCl, anhydrous HF was employed in the hydrolysis of cellulose. The main advantage of using anhydrous HF is its low boiling point (19.5 °C) which facilitated the acid recovery. The yield of sugars was about 45% at 0 °C. The recovery experiment showed that only 0.05–0.1% of HF remained in the system, opening the possibility of reusing mineral acids in the hydrolysis of cellulose.

Current strategies for the hydrolysis of cellulose with acids are mainly accomplished with the acids mentioned above. Although homogeneous-based processes are efficient, the mineral acid systems still suffer from major problems in product/catalyst separation, reactor corrosion, catalyst recycling and the treatment of waste effluent. For example, in the H2SO4 based system, the acid in the reaction mixture has to be neutralized with a mixture of CaO/CaSO4 which forms lots of gypsum as waste. For the HCl system it is difficult to reuse the liquid acid while the HF system is very toxic when utilized in large-scale processes. In the search for greener processes for hydrolyzing cellulose, solid acids were developed to address some of the problems and have some unique catalytic properties that mineral acids do not possess.

4. Hydrolysis of cellulose by solid acids

The hydrolysis of cellulose into sugars with solid acids has received increasing attention. Solid acid catalysts have various advantages over liquid acid catalysts: ease of product separation, recyclability, less damage to the reactor. Besides, the use of solid acid catalysts can reduce the pollutants which will have a minimal impact on the environment. Up till now, numerous reviews have been published on the transformation of cellulose with solid acids. Herein, we would like to summarize the recent advances in this subject. Several types of solid acids are included in the following part and their catalytic performance is summarized in Table 1.

4.1 Metal oxides

Metal oxides are a type of solid catalyst with many Lewis acid sites. Metal oxides are always prepared with high specific surface and pore sizes which are easy for the reactants to access and contact with the active sites inside the metal oxide pores. These metal oxides can be used for the hydrolysis of sucrose, cellobiose and even cellulose.

As a type of strong solid acid, mesoporous transition-metal oxides have been prepared and used in organic chemical transformations. Recently, Domen et al. reported that mesoporous Nb–W oxide could be used as a solid catalyst for the hydrolysis of sucrose and cellobiose. The rate of glucose production and the turnover frequency (TOF) for the hydrolysis of sucrose were higher than those of other solid acids (i.e. Amberlyst-15, Nb2O5). The acid strength increased gradually with the addition of W, reaching the highest reaction rate with mesoporous Nb3W7 oxide. The high catalytic performance of Nb3W7 oxide was attributed to the high surface area mesoporous structure and strong acid sites. However, the Nb–W oxide catalyst had a lower activity for the cellobiose hydrolysis due to the low Bronsted acid sites.

In order to solve the problem, Domen et al. also reported a layered transition-metal oxide H Nb Mo O that exhibited...
remarkable catalytic performance for the hydrolysis of sucrose, cellobiose, starch and cellulose (Scheme 3). For the hydrolysis of sucrose and cellobiose, the layered H NbMoO 6 catalyst exhibited the highest activity, producing glucose at twice the rate of Amberlyst-15 (Fig. 1). The high activity of H NbMoO 6 in these reactions was attributed to its strong acidity, water-tolerance and intercalation ability. The XRD patterns and FT-IR spectrum of H NbMoO 6 immersed with glucose, sucrose and cellobiose, revealed that the saccharide was successfully intercalated into the interlayer gallery. However, the total yield of the products (glucose and cellobiose) was only 8.5% in the hydrolysis of cellulose (Fig. 2). Thus, increasing the acid site density and the surface area of a layered transition-metal oxide is necessary for the full conversion of cellulose to sugars.

In addition, nanoscale metal oxide catalysts have the potential to improve the catalytic performance of the hydrolysis reaction. Fang et al. 64 used nano Zn–Ca–Fe oxide as the catalyst in the crystalline cellulose hydrolysis reaction. The catalyst exhibited good catalytic activities. The cellulose conversion and the glucose selectivity were 42.6% and 69.2%, respectively. Nano Zn–Ca–Fe oxide gave better performances with respect to hydrolysis rates and glucose yields than fine particle Zn–Ca–Fe. Besides, the paramagnetic nature of Fe oxides made it easy to separate the nano Zn–Ca–Fe oxide from the reaction mixture by simple magnetic filtration techniques.

4.2 Polymer based acids
Polymer based acids with Brønsted acid sites have been used as effective solid catalysts for many organic reactions including hydrolysis reactions. 65–67 Macrocyclic cellulose resins with sulfonic groups (–SO 3 H) are one of these polymer based acids, known as Amberlyst. They are commercially available, inexpensive and stable in most solvents. The macroporous structures of these acids allow small molecules to enter into the pores and interact with more active acid sites.

Recent pioneering work on the hydrolysis of microcrystalline cellulose and α-cellulose with Amberlyst 15DRY resin was reported by Schüth et al. 68 Purified cellulosic substrates were dissolved in 1-butyl-3-methylimidazolium chloride ([BMIm]Cl) in order to increase their solubility and make the transport of cellulose chains to the acid sites a highly demanding process. After hydrolysis with Amberlyst 15DRY, cellulosic materials were selectively converted to cello-oligomers or sugars. As the reaction proceeded, the hydrolysis performances using Amberlyst 15DRY showed an induction period of about 1.5 h (Fig. 3). However, when soluble p-toluenesulfonic acid (p-TSA) was used, resembling the acid sites of Amberlyst 15DRY, no induction period was given during the first 1.5 h. HPLC analysis of the reducing sugars showed that almost no mono- and disaccharides were produced during the initial 1.5 h, while the production of small sugars was detected for the reaction catalyzed by p-TSA. The difference of the two systems was investigated by...
the visual appearance of isolated cellulose suspensions and degree of polymerization (DP) analysis. The recovered cellulose from the ionic liquid appeared in different forms with the reaction variation (Fig. 4). The isolated cellulose became smaller with increasing reaction time, giving a colloidal dispersion after 5 h of reaction. The figure shows that there were substantial changes in the cellulose structure. The degree of polymerization (DP) analysis of cellulose at different reaction times also demonstrated that cellulose was effectively depolymerized in the presence of Amberlyst 15DRY. It was worth noting that cello-oligomers with a DP of around 30 were found after 1.3 h of hydrolysis of microcrystalline cellulose and could be precipitated in 90% yield. No fermentable sugars were detected during the first 1.5 h which was in accordance with the induction time observed in Fig. 4. Since the high solubility of sugars in ionic-liquid made the sugar extraction and ionic liquid recovery very difficult, the route gave a cello-oligomer production method instead of total hydrolysis into fermentable sugars which was an advantage of this process. Further extension of the reaction time led to the production of sugars and some dehydration products. The most appealing part of the route was that it can selectively convert cellulose or even wood into cello-oligomers, which could be further broken down into sugars. The hydrolysis reaction proceeded in the cellulose → cello-oligomers → sugars → dehydration products series, and if the process was properly terminated at different times, cellulose fragments or sugars could be selectively obtained for different use in biorefineries.

In order to gain more insight into the controlling factors in hydrolysis reactions, Rinaldi and Schüth et al.69 investigated the effect of different parameters on the hydrolysis of cellulose in [BMMim]Cl with Amberlyst 15DRY such as acid amount, reaction temperature and impurities. They found that depolymerization is a first-order reaction with respect to catalyst concentration. Particularly, they discovered that the induction period depends heavily on the amount of acid used for the reaction (Fig. 5). Increase of catalyst concentration from 0.46 to 6.9 mmol of \( \text{H}_2\text{SO}_4 \) decreased the induction time from 1.9 h to less than 5 min. This means that the acid concentration played an important role in the hydrolysis reaction, and the use of a larger amount of Amberlyst 15DRY resembling the use of a soluble strong acid showed no induction period for the production of glucose. The activation energy for the depolymerization of cellulose is 108 kJ mol\(^{-1}\), which is relatively lower than that with liquid acid (i.e. \( \text{H}_2\text{SO}_4 \) 170 kJ mol\(^{-1}\)).

Compared to the enzymatic hydrolysis of cellulose, the solid or liquid acid catalyzed depolymerization of cellulose always requires higher temperature due to its higher reaction activation energy. It was reported that the activation energy for cellulose hydrolysis with dilute acid is 170–180 kJ mol\(^{-1}\) (no matter what temperature and acid concentration are used).70 On the other hand, the activation energy for enzymatic hydrolysis is only 3–50 kJ mol\(^{-1}\), resulting in the hydrolysis reaction being conducted at the low temperature of 50 °C.71–73 An ideal cellulose-mimetic catalyst consisting of a cellulose-binding domain and a catalytic domain was developed for cellulose hydrolysis by Pan’s research group.74 The catalyst contained a chloride (–Cl) group which plays the cellulose-binding role by forming hydrogen bonds, and sulfonic acid groups (–SO\(_3\)H) functioning as the hydrolytic domains. Chloromethyl polystyrene (CP) resin with –Cl groups was chosen as the catalyst support. The –SO\(_3\)H groups were introduced by partially substituting –Cl groups with sulfanilic acid. The proposed mechanism of cellulose hydrolysis is shown in Scheme 4. The catalyst was firstly applied to the hydrolysis of cellobiose. It was completely hydrolyzed to glucose at 120 °C over 2 h, while only 8% of cellobiose was obtained with sulfuric acid under the same conditions. Adsorption experiments showed that CP–SO\(_3\)H adsorbed both glucose and cellobiose through hydrogen binding between the chloride groups on the catalyst and the hydroxyl groups of the sugars (Fig. 6). The preferable adsorption of cellobiose over glucose is critical for cellobiose hydrolysis to proceed which ensures the desorption of glucose product from the catalyst. CP–SO\(_3\)H showed excellent catalytic performance for the hydrolysis of crystalline cellulose (Avicel). The best yield of glucose from CP–SO\(_3\)H was up to 93%, while almost no Avicel was hydrolyzed on using sulfuric acid. The activation energy of cellulose hydrolysis catalyzed by CP–SO\(_3\)H was 83 kJ mol\(^{-1}\) at 373–413 K and is much lower than that of sulfuric acid (170 kJ mol\(^{-1}\)) or sulfonated active carbon (AC–SO\(_3\)H) (110 kJ mol\(^{-1}\)).75 This was the key point as to why the hydrolysis reaction could be conducted at lower temperature.
Apart from the Amberlyst-type resins, Nafion (sulfonated tetrafluoroethylene based fluoropolymer-copolymer) was another type of effective solid acid for the hydrolysis of cellulose. Suh et al. developed a cellulose pretreatment process using [BMIm]Cl before the subsequent hydrolysis over Nafion NR50. The pretreatment step was to decrease the crystallinity of cellulose. The hydrolysis of regenerated cellulose (from the pretreatment of cellulose with [BMIm]Cl) yielded 35% glucose. Moreover, Lucht et al. reported the hydrolysis of cellulose by a Nafion supported on amorphous silica (Nafion SAC 13) catalyst under mild conditions. The catalyst had the potential to be recycled or applied in a continuous flow reactor. It showed excellent performance in the hydrolysis of cellobiose; 100% glucose was obtained at 130 °C over 24 h. The hydrolysis of cellulose needed a higher temperature (190 °C); the yield of glucose was 11% for the first time. The catalyst provided 8% and 7% yields of glucose for the second and third reaction runs, which suggested it to be a recyclable catalyst for the conversion of cellulose into useful chemicals in the future.

Porous coordination polymers (PCPs) are a new class of porous solids with a large variety of pore surfaces and pore structures. Recently, it was demonstrated by Akiyama et al. that PCPs decorated with sulfonic acid groups could be used as catalysts for cellulose hydrolysis. MIL-101, composed of a chromium oxide cluster and terephthalate ligand, was chosen as the platform to introduce the –SO3H groups, and the BET surface area was 1915 m² g⁻¹ (Scheme 5). The hydrolysis reaction was carried out at 393 K over 3 h and produced 2.6% 1.4% and 1.2% yields of xylose, glucose and cellobiose, respectively. By increasing the reaction time, the yields of these sugars increased. The merit of this new catalyst is that it prevents the formation of side-products such as 5-hydroxymethylfurfural or levulinic acid which are normally found in the hydrolysis of cellulose under strong acidic conditions. However, it was hard for cellulose to diffuse deep inside the porous solid due to the large size of cellulose. Since cellulose is a crystal and insoluble in water, it is assumed that only one end of the cellulose chain diffused into the pores and had contact with the acidic sites, leading to a clean cut of the chain. The reuse experiments of the PCPs catalyst showed no decrease in the catalytic activity after testing 13 times, indicating that it was a highly stable catalyst for the hydrolysis reaction.

4.3 Sulfonated carbonaceous based acids

Among various types of solid acid for the hydrolysis of cellulose, carbonaceous solid acids have superior catalytic activities. The good recyclability and cheap naturally occurring raw materials of these carbonaceous acids make them better candidates for the production of biofuel precursors. The first carbonaceous acids from sulfonated D-glucose/sucrose materials were reported by Hara et al. D-Glucose and sucrose were incompletely carbonized at low temperature to form small polycyclic aromatic carbon rings and subsequently sulfonated with sulfuric acid to introduce sulfonic groups (–SO3H). They used the carbonaceous acids for the transesterification of vegetable oils to biofuels. After their work, much attention was paid to these new types of amorphous solid acid which could be used as catalysts for the cellulose hydrolysis reaction.

Carbon-based solid acids were prepared by sulfonation of incompletely carbonized natural polymers, such as sugars, cellulose and starch or by incomplete carbonization of sulfopoly cyclic aromatic compounds in conc. H₂SO₄. Hara et al. reported the preparation method of carbon material bearing...
-SO₃H groups from microcrystalline cellulose at 723 K over 5 h under N₂ flow. The black powder was then boiled in 15 wt% H₂SO₄ at 353 K under N₂ for 10 h; after filtration and washing with hot water, carbon based acid was obtained. Characterization of this solid acid showed that the carbon material is composed of uniform functionalized graphene sheets, bearing -SO₃H, -COOH and phenolic -OH groups which are different to conventional solid acids with single functional groups (Scheme 6). The effective surface area of the carbon material during hydrolysis was about 560 m² g⁻¹, larger than the BET surface area after hydrolysis (only 2 m² g⁻¹). The H₂O vapor adsorption-desorption isotherm showed that a larger amount of water was incorporated into the bulk of the catalyst. The incorporation ability of hydrophilic molecules made it easy for a cellulose chain in solution to be in contact with the -SO₃H groups in the carbon material, which gave rise to high catalytic performance.

Comparable experiments for the hydrolysis of cellulose with different solid acids revealed that carbon-based acids exhibit remarkable hydrolysis performances (Table 2). After reacting for 3 h, 68% of cellulose was hydrolyzed to glucose (4% yield) and soluble β-1,4-glucan (64% yield), the liquid acid H₂SO₄ also has a high activity for the hydrolysis of cellulose (10% glucose and 38% β-1,4-glucan). The enhanced hydrolytic catalysis of the amorphous carbon with -SO₃H, -OH and -COOH and was further investigated via an adsorption experiment with cellulose, a short β-1,4-glucan of cellulose. The results showed that the strong interactions (hydrogen bonds to oxygen atoms in glycosidic bonds) between the phenolic OH groups and the glycosidic bonds in β-1,4-glucan led to higher catalytic activities. Such hydrogen bonds were expected to bind cellulose to the surface of the catalysts, making it easier for the hydrolysis to proceed. The activation energy for cellulose hydrolysis with this carbon based acid was 110 kJ mol⁻¹ which was lower than that with sulfuric acid (170 kJ mol⁻¹). The amorphous carbon acid was recovered from the reaction mixture and reused at least 25 times without decrease in activity. Elemental analysis and ion chromatography revealed that only 1% -SO₃H groups leached into the solution during the first reaction and no further leaching was detected in subsequent reactions. The excellent performance of the carbon based catalyst opens the possibility of converting cellulose into value-added molecules with cheap and efficient solid acids, which has the potential for use in industrial production in the future.

A mild process for the hydrolysis of cellulose to reducing sugars under microwave irradiation was developed by Fu and Yin et al. They used carbon sulfuric acids (BC-SO₃H) derived from bamboo, cotton and starch as catalysts. The introduction of microwave irradiation greatly accelerated the rate of the hydrolysis reaction. Comparison of hydrolysis results between the two heating methods over BC-SO₃H revealed that the accelerating effect of microwave irradiation on the reaction was evident. The hydrolysis reaction operated at a lower temperature of 70–100 °C and the yield of reducing sugars was higher than that using conventional heating. The yields of hydrolysis products were different with the different types of carbon acids. The correlation between the hydrolysis product yields and adsorption values confirmed the results from Hara’s work that the adsorption of the phenolic OH groups of BC-SO₃H to the oxygen atoms in the β-1,4-glycosidic bonds was responsible for the high catalytic activities of these carbon-based solid acids when hydrolyzing cellulose to glucose.

Carbonaceous solid acid (CSA) can also be applied to real biomass substrates under microwave irradiation. The Jiang and Mu research group illustrated that lignocellulosic biomass (e.g. corn cob) can be well hydrolyzed by self-derived CSA under microwave irradiation. The CSA was prepared from hydrolyzed corn cob residue and was used for the hydrolysis of

![Scheme 6](image)

**Scheme 6** Schematic structure of the carbon-based solid acid. (Reproduced from ref. 82a.)

| Catalyst       | Functional groups | Density (mmol g⁻¹) | Max. acidity H₀ | Surface area (m² g⁻¹) | Yields of hydrolysis products                                                                 
<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>H₂SO₄</td>
<td></td>
<td>20.4</td>
<td>−11</td>
<td>−11</td>
<td>Glucose: 10%, β-1,4-glucan: 38%</td>
</tr>
<tr>
<td>Niobic acid</td>
<td>Acidic OH</td>
<td>0.4</td>
<td>−5.6</td>
<td>90</td>
<td>Glucose: 10%, β-1,4-glucan: 38%</td>
</tr>
<tr>
<td>H-mordenite</td>
<td>Acidic OH</td>
<td>3.4</td>
<td>−5.6</td>
<td>480</td>
<td>Glucose: 10%, β-1,4-glucan: 38%</td>
</tr>
<tr>
<td>Nafion SO₃H</td>
<td></td>
<td>0.9</td>
<td>−11 to −13</td>
<td>&lt;1</td>
<td>Glucose: 10%, β-1,4-glucan: 38%</td>
</tr>
<tr>
<td>Amberlyst-15</td>
<td>SO₃H</td>
<td>4.8</td>
<td>−2.2</td>
<td>50</td>
<td>Glucose: 4%, β-1,4-glucan: 64%</td>
</tr>
<tr>
<td>Carbon material</td>
<td>COOH</td>
<td>1.9</td>
<td>−8 to −11</td>
<td>2</td>
<td>Glucose: 4%, β-1,4-glucan: 64%</td>
</tr>
<tr>
<td></td>
<td>Phenolic OH</td>
<td>2.0</td>
<td>−11</td>
<td>−11</td>
<td>Glucose: 10%, β-1,4-glucan: 38%</td>
</tr>
</tbody>
</table>

* Conditions: catalyst 0.3 g, cellulose 25 mg, H₂O 0.7 g, 3 h.
corncob (Scheme 7). In this way, the whole corncob could be utilized in the process and two products were obtained that were sugars (from the cellulose and hemicelluloses part) and CSA (from the unconverted solid residue). The hydrolysis reactions produced 78% yield of xylose and arabinose at 403 K. The effective utilization of the hydrolyzed residues reduces the cost of the catalysts and pollution.

Apart from microwave irradiation, ionic liquids were also investigated as effective solvents for the hydrolysis of cellulose with glucose derived sulfonated carbon acid, reported by Qi et al. (Scheme 8).85 Cellulose has good solubility in the ionic liquid which enables easier contact with more acid sites. When the reaction was conducted at 110 °C, the total reducing sugars yield was up to 72.7%. Further increase in the reaction temperature led to an increase reaction rates but decreased the TRS yield, due to the rapid decomposition of the formed sugars at higher temperature.

Whereas much effort has been invested in the optimization of the hydrolysis reaction conditions of cellulose over carbon-based solid acids, the sulfonation conditions have rarely been considered. Recently, Zhang et al.86 reported that by changing the sulfonation temperature of the active carbon (AC), the catalyst exhibited different catalytic activities in the hydrolysis reaction. The active carbon was treated with/without nitric acid and sulfonated at different temperature ranging from 150–300 °C. With the increase of the sulfonation temperature, the acid density of the sulfonated carbon increased. The specific areas of the samples were increased when the temperature was increased from 150 to 250 °C, but decreased on further increasing the temperature. The hydrolysis of ball-milled cellulose was conducted at 150 °C over these solid acids and the AC–N–SO₃H sulfonated at 250 °C gave the best performance; the cellulose conversion and glucose yield were 74.3% and 62.6%, respectively. Apart from the sulfonation conditions, the carbon sources were also evaluated. Among the tested carbons, CMK-3, a type of ordered mesoporous material, gave the best performance with a cellulose conversion of 94.4% and a glucose yield of 74.5% which is the highest glucose yield achieved via catalysis by carbon based solid acids until now. The sulfonated CMK-3 material has a higher acid density and surface area (412 m² g⁻¹); both parameters are important for cellulose conversion.

A new class of sulfonated silica/carbon nanocomposite catalyst was reported by Jacobs and Sels et al. for the hydrolysis of ball-milled cellulose to sugars.87 The sample was prepared by evaporation of a sucrose/TEOS/F127 solution (carbon source/silica precursor/structure-directing amphiphilic surfactant) and followed by carbonization in N₂ to decompose F127 and convert the sucrase into carbon residues. The resulting hybrid materials were finally treated with sulfuric acid to obtain sulfonated silica/carbon nanocomposites. As the carbonization temperature varied, the ratio of the Si and C in the samples changed, denoted as SiₘCₙ-T-SO₃H (m, n are the weight percentages of silica and carbon, T is the carbonization temperature). The catalysts exhibited good performances in the hydrolysis reaction. The Si₃₃C₆₆-823-SO₃H catalyst resulted in the highest glucose yield of 50% (Fig. 7). The hybrid surface structure facilitated the adsorption of β-1,4-glucan on the solid acid, and together with the strong accessible Brønsted acid sites suggested that the sulfonated silica/carbon nanocomposites...
have potential for the selective hydrolysis of cellulose to glucose.

### 4.4 Heteropoly acids

Heteropoly acids (HPAs) are a type of solid acid, consisting of early transition metal–oxygen anion clusters, and they are usually used as a recyclable acid in chemical transformations.\(^8\) The most common and widely used heteropoly acids are Keggin type acids with the formula \([XY_M\{12-x\}O_{40}]^-\) (X is the heteroatom and M and Y are addendum atoms). Heteropoly acids have received much attention due to their fascinating architectures and excellent physicochemical properties such as Brønsted acidity, high proton mobility and good stability.\(^9\)–\(^12\) They dissolve in polar solvents and release \(H^+\), whose acidic strength is stronger than typical mineral acids such as sulfuric acid.\(^14\) However, the Keggin type acids cannot be used as heterogeneous catalysts in polar solvents. The substitution of protons with larger monovalent cations such as \(Cs^+\) gives solid catalysts that are insoluble in water and other polar solvents.\(^15\) For example, \(Cs_xH_{12-x}PW_{12}O_{40}\) was used as a heterogeneous catalyst with strong acidity and large surface area. Heteropoly acids have been widely used in catalytic systems for biomass conversion.\(^16\) Recently, they exhibited excellent performances in the hydrolysis of cellulose to glucose. After extraction with organic solvents, the heteropoly acids could be separated from the homogeneous solution and dried for the next use.

Shimizu et al.\(^7\) reported heteropoly acid (\(H_3PW_{12}O_{40}\) and \(HSiW_{12}O_{40}\)) and metal salt (\(M_x\{PW_{12}O_{40}\}, M = cation\)) catalysts for the hydrolysis of cellobiose and ball-milled cellulose into glucose or sugars. Comparison experiments on the hydrolysis of cellulose with different acids (heteropoly acids and mineral acids) revealed that the heteropoly acids show better hydrolysis activity effects than mineral acids. The total reducing sugars yield decreased in the following order: \(H_3PW_{12}O_{40} > HSiW_{12}O_{40} > HClO_4 > H_2SO_4 > H_3PO_4\). The hydrolysis reaction using \(H_3PW_{12}O_{40}\) provided TRS and glucose in 18% and 15% yields, respectively. The conversion of cellulose, and TRS yield correspond well to the deprotonation enthalpy (DEP) of these Bronsted acids, such that a stronger Bronsted acid is more favorable for the hydrolysis of \(\beta\)-1,4-glycosidic bonds in cellulose (Fig. 8). They also used salts of \(PW_{12}O_{40}\) (\(Ag^+\), \(Ca^{2+}\), \(Co^{3+}\), \(Y^{3+}\), \(Sn^{4+}\), \(Sc^{3+}\), \(Ru^{3+}\), \(Fe^{3+}\), \(Hf^{4+}\), \(Ga^{3+}\) and \(Al^{3+}\)) for the hydrolysis of cellulose. The turnover frequencies (TOFs) for cellulose conversion and TRS formation first increased with the \(e/r\) values (ratio of charge and ionic radius) and then decreased. Maximum TOFs for both cellulose conversion and TRS formation were achieved with moderate Lewis acidity (\(e/r\) values) such as for \(Sn_{0.25}PW_{12}O_{40}\).

Wang et al.\(^8\) reported the optimization of the hydrolysis reaction conditions with the \(H_3PW_{12}O_{40}\) catalyst such as reaction time, temperature and the amount of cellulose. Microcrystalline cellulose was selected as the starting material. A higher glucose yield of \(>50%\) was obtained with a selectivity of \(>90%\) at \(453\) K over \(2\) h. In their recycling experiments, the \(H_3PW_{12}O_{40}\) was extracted from the solution with diethyl ether.

The total loss of catalyst after six runs was \(8.8%\) of the starting amount of \(H_3PW_{12}O_{40}\).

Apart from the heteropoly acids mentioned above, many other heteropoly acids have also been developed to catalyze the hydrolysis reaction. Mizuno et al.\(^9\) reported that highly negatively charged heteropoly acids, particularly \(H_3BW_{12}O_{40}\), have stronger acidity than \(H_3PW_{12}O_{40}\) for the hydrolysis of non-pre-treated crystalline cellulose into saccharides under mild reaction conditions. The HPAs, \(H_3BW_{12}O_{40}\), \(H_3AlW_{12}O_{40}\), and \(H_3GaW_{12}O_{40}\) gave different performances and afforded watersoluble saccharides such as glucose and cellobiose (Table 3). Among these HPAs, \(H_3BW_{12}O_{40}\) gave the highest glucose yield of \(77%\). The hydrolysis activities of these HPAs were better than Keggin type acids and conventionally utilized \(H_2SO_4\) and HCl. It was worth mentioning that the highly negatively charged heteropoly acid solution was a better “cellulose-solvent” with strong hydrogen-bond accepting abilities due to the external metal–oxygen clusters from the anions. When the crystalline cellulose was immersed in an aqueous solution of \(Na_2BW_{12}O_{40}\) at room temperature for \(72\) h, the crystallinity of cellulose decreased. The crystalline peaks almost disappeared after crystalline cellulose was immersed in an aqueous solution of \(H_3BW_{12}O_{40}\) at \(20\) °C for \(24\) h, while not much change was found in the crystallinity on treatment with \(H_2SO_4\) and HCl solutions. These results show that the hydrogen bond accepting ability of \(H_3BW_{12}O_{40}\) leading to a decrease in the crystallinity of cellulose is another factor in the high catalytic performance beyond the strong acidity. \(H_3BW_{12}O_{40}\) was also used for the hydrolysis of natural lignocellulosic biomass such as rice plant and Japanese cedar and a mixture of saccharides with high yields (>77%) was obtained.

![Fig. 8 Effect of deprotonation enthalpy of acid catalyst on (○) TRS yield and (●) cellulose conversion, for cellulose hydrolysis at 423 K over 2 h. (Reproduced from ref. 97.)](image-url)
As is known, the hydrolysis of cellulose is always restricted by the poor contact between a catalyst and cellulose. The hydrolysis reactions always require higher catalyst/substrate mass ratios, higher temperature and longer reaction times to achieve maximum conversion, but lead to a lower selectivity to glucose and lots of side products. Much work has focused on developing effective approaches or technologies for the hydrolysis of cellulose. By using heteropoly acids under microwave irradiation, reported by the Mu research group, crystalline cellulose was completely converted with a high selectivity to glucose at lower temperature (80–100 °C). The best result for glucose (75.6%) was obtained by using 88% of H3PW12O40 solution as a catalyst at 90 °C for 3 h. Furthermore, the system could be applied to the hydrolysis of real lignocellulosic biomass such as corn cob, corn stover and bagasse; 37.2%, 43.3% and 27.8% yields of glucose were obtained, respectively. Another appealing route was the development of micellar heteropoly acid catalyst [C16H33N(CH3)3]H2PW12O40 with a surfactant group. The catalyst was demonstrated to be effective, and the conversion of cellulose was 55.1% with a 36% yield of glucose in a water miscible solvent (2 mL), 60 °C. Crystalline cellulose was immersed in the solution at room temperature for 24 h, and then the mixture was heated at 60 °C for 48 h. Yields are based on the glucose unit in cellulose used. The proton concentration was adjusted using H2SO4.

Table 3 Saccharification of crystalline cellulose in aqueous acidic media† (ref. 99)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Acid</th>
<th>Concentration [mol L⁻¹]</th>
<th>Anion</th>
<th>Proton</th>
<th>Glucose</th>
<th>Cellobiose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H3PW12O40</td>
<td>0.70</td>
<td>2.1</td>
<td>8</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>H3PW12O40</td>
<td>0.60</td>
<td>3.5</td>
<td>18</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>H3SiW12O40</td>
<td>0.70</td>
<td>2.8</td>
<td>37</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>H3SiW12O40</td>
<td>0.70</td>
<td>3.5</td>
<td>61</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>H3PW12O40</td>
<td>0.70</td>
<td>3.5</td>
<td>77</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>H3PW12O40</td>
<td>0.40</td>
<td>2.0</td>
<td>4</td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>H3PW12O40</td>
<td>0.70</td>
<td>3.5</td>
<td>68</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>H3GaW12O40</td>
<td>0.70</td>
<td>3.5</td>
<td>62</td>
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<td></td>
</tr>
<tr>
<td>9</td>
<td>H3CoW12O40</td>
<td>0.70</td>
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<tr>
<td>10</td>
<td>H3SO4</td>
<td>1.75</td>
<td>3.5</td>
<td>1</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>HCl</td>
<td>3.5</td>
<td>3.5</td>
<td>4</td>
<td>nd</td>
<td></td>
</tr>
</tbody>
</table>

† Reaction conditions: crystalline cellulose (100 mg), aqueous acidic solution (2 mL), 60 °C. Crystalline cellulose was immersed in the solution at room temperature for 24 h, and then the mixture was heated at 60 °C for 48 h. Yields are based on the glucose unit in cellulose used. The proton concentration was adjusted using H2SO4.

H-form zeolites are microporous, aluminosilicate minerals that are commonly used in petrochemistry. They are non-toxic and easy to recover from solution. They have porous structure that can accommodate a wide variety of cations, such as H⁺, Na⁺, K⁺, Mg²⁺. These cations are loosely bonded to the zeolite surface and can be released into solution to exhibit different catalytic activities. H-form zeolites are widely used acid catalysts due to their shape-selective properties in chemical reactions. The acidity is related to the atomic ratio of Si/Al; the amount of Al atoms is proportional to the amount of Brønsted acid sites, the higher the ratio of Al/Si, the higher the acidity of the catalyst.

Onda et al. reported the hydrolysis of cellulose with different types of solid acids in water. H-form zeolites with various structures and Si/Al ratios were included. However, the zeolite catalysts with high Si/Al ratio, such as H-beta (75) and H-ZSM (45), showed higher activities than those with lower Si/Al ratio such as H-beta (13) and H-mordenite (10) for glucose, which was in contrast to the acidity density of zeolites. This may due to the highly hydrophobic character of zeolites with high Si/Al ratios. The glucose yield was relatively low compared to AC-SO₃H which was about 12%. It may due to the small pore diameters of zeolites that limited the accessibility and their weak and less acidic sites. In order to further improve the catalytic activities of zeolites under milder conditions, Zhao and Zhang proposed a new route by using an ionic liquid as the solvent to increase the solubility of cellulose, improving the contact between cellulose and zeolites. Besides, microwave irradiation (MI) was used to accelerate the hydrolysis rates. Among the tested zeolites, HY zeolite, with the lowest Si/Al molar ratio, showed the best hydrolysis performance at 240 W in 8 min (TRS yield was 47.5% with a glucose yield of 36.9%) (Table 4). The higher MI power led to the formation of 5-hydroxymethylfurfural (HMF) (~49% yield under MI power of 400 W) through consecutive elimination of water during the hydrolysis of cellulose. Compared with the conventional heating manner in an oil bath, the TRS yield using microwave irradiation heating was almost four times that obtained using oil bath heating. The results strengthened the evidence that proper solvents and heating methods could greatly improve the reaction efficiency over solid acids. Finally, application of this method to other cellulose samples with different origins or with different degrees of polymerization (DP) also succeeded (Table 5). The higher the DP value of cellulose, the longer the microwave heating time that was required to reach the maximal TRS yield. When the DP value increased, the yields of TRS and glucose dropped slightly.

Further insight into the mutual behavior of zeolites in ionic liquids was gained by Zhang et al. By using XRD characterization, they found that the framework structure of a zeolite is stable while the enlargement of cell parameters takes place due to the dilatation effect of an ionic liquid. [BMIm]Cl

4.5 H-form zeolites

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Green Chem., 2013, 15, 1095–1111 | 1105
lyzed cellulose hydrolysis in IL (Scheme 9). First, the [BMIM]+

catalysts from the hydrolysis solid residue is important for
difficult to separate from the

Table 4 The results of the solid acid-catalyzed hydrolysis of Avicel cellulosea
(ref. 106)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time/min</th>
<th>Yield of glucose</th>
<th>Yields of TRS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HY</td>
<td>600</td>
<td>2.1</td>
<td>7.1</td>
</tr>
<tr>
<td>2</td>
<td>HY</td>
<td>4</td>
<td>20.8</td>
<td>23.4</td>
</tr>
<tr>
<td>3</td>
<td>HY</td>
<td>8</td>
<td>36.9</td>
<td>47.5</td>
</tr>
<tr>
<td>4</td>
<td>HY</td>
<td>15</td>
<td>24.2</td>
<td>34.8</td>
</tr>
<tr>
<td>5</td>
<td>HZSM-5a</td>
<td>9.5</td>
<td>35.2</td>
<td>42.9</td>
</tr>
<tr>
<td>6</td>
<td>HZSM-5b</td>
<td>9.5</td>
<td>33.7</td>
<td>45.3</td>
</tr>
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<td>7</td>
<td>H-beta</td>
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<td>NKC-9</td>
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</tr>
<tr>
<td>9</td>
<td>HY</td>
<td>8</td>
<td>4.5</td>
<td>12.7</td>
</tr>
<tr>
<td>10</td>
<td>—</td>
<td>8</td>
<td>7.1</td>
<td>18.8</td>
</tr>
</tbody>
</table>

Table 5 Results of HY zeolite-catalyzed hydrolysis of different cellulose samples (ref. 106)a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cellulose type</th>
<th>DP</th>
<th>Time/min</th>
<th>Glucose yield</th>
<th>TRS yields</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>α-Cellulose</td>
<td>100</td>
<td>7</td>
<td>34.9</td>
<td>46.5</td>
</tr>
<tr>
<td>2</td>
<td>Avicel cellulose</td>
<td>220</td>
<td>8</td>
<td>36.9</td>
<td>47.5</td>
</tr>
<tr>
<td>3</td>
<td>Spruce cellulose</td>
<td>275</td>
<td>9</td>
<td>34.5</td>
<td>44.4</td>
</tr>
<tr>
<td>4</td>
<td>Sigmacell cellulose</td>
<td>450</td>
<td>9.5</td>
<td>32.5</td>
<td>42.4</td>
</tr>
<tr>
<td>5</td>
<td>Cellulose</td>
<td>1440</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

4.6 Magnetic solid acids

As for the real biomass feedstock and practical process for the hydrolysis of cellulose to glucose, a challenge still exists with respect to the transformation system. Solid catalysts cannot be directly separated when solid residues are formed during the hydrolysis process. Although cellulose can be degraded into soluble sugars, the lignin components of the actual cellulose biomass cannot be converted and humins sometimes form as solid residues, both of which are difficult to separate from the recovered solid catalysts. Additionally, the separation of catalysts from the hydrolysis solid residue is important for the analysis of the recovered catalyst which may be related to the explanation of the catalytic mechanism. To address the problem, we developed magnetic sulfonated mesoporous silica (SBA-15), which can be successfully separated from the reaction system with a permanent magnet, in our recent work.108,109

The magnetic solid acid was prepared by a surfactant-templated sol–gel method similar to reported methods.110,111 Fe3O4 magnetic nanoparticles were dispersed in the block copolymer P123 for the co-condensation of tetraethoxysilane (TEOS). After assembly, 3-(mercaptopropyl)trimethoxysilane (MPTMS) was added to introduce mercapto groups. H2O2 was used to oxidize the mercapto groups into sulfonic acid groups inside the pores of the mesoporous silica. X-Ray photoelectron spectroscopy (XPS) analysis of the sample showed that there was only one peak (169.01 eV) between 158–177 eV in binding energy, demonstrating that the sulfur element in the catalyst was completely in the form of sulfonic acid groups (Scheme 10).

Experiments on the hydrolysis of cellobiose with Fe3O4–SBA–SO3H showed that the magnetic solid acid gave an even better performance than sulfuric acid. A proposed explanation was that the channels in the magnetic solid acid contain concentrated acid sites and the uniform channels allow the reactants to easily enter and interact with these acid sites. Further hydrolysis of amorphous cellulose (pretreated with 1-butyl-3-methylimidazolium chloride) with Fe3O4–SBA–SO3H gave a 50% yield of glucose. The protons diffused from the SBA-15 channels on the surface of cellulose undergo hydrolysis reaction. When the magnetic solid acid was used for the hydrolysis of microcrystalline cellulose, the yield of glucose decreased to 26%. Comparative studies revealed that Fe3O4–SBA–SO3H exhibited an even better hydrolysis performance than AC–SO3H and Amberlyst-15, presumably due to its higher surface...
area. Also, when corncob was used as lignocellulose biomass for a hydrolysis reaction, the total reducing sugar (TRS) yield was 45% (Fig. 9).

The catalyst separation is presented in Scheme 11. The used Fe\textsubscript{3}O\textsubscript{4}–SBA–SO\textsubscript{3}H can be easily separated from the reaction mixture by using a permanent magnet. The recycled catalyst was washed with 1 M H\textsubscript{2}SO\textsubscript{4} and water/ethanol, and dried at 80 °C for the next use without deactivation. TEM, XRD and BET analysis of the used catalyst revealed that the mesoporous structure is retained and the Fe\textsubscript{3}O\textsubscript{4}–SBA–SO\textsubscript{3}H is robust in the hydrothermal conditions.

Another appealing work based on a magnetic solid acid was reported by Ebitani et al.\textsuperscript{112} The catalyst was prepared by using CoFe\textsubscript{2}O\textsubscript{4} as the magnetic core and embedded with silica, followed by oxidation of thiol groups to –SO\textsubscript{3}H groups. It was a highly active catalyst for the hydrolysis of disaccharides and polysaccharides. The use of nanoparticles was expected to overcome the difficulty of the solid–solid reaction and they were well dispersed in water solution. By introducing magnetic parts in the catalyst, it can be easily separated from solution. The hydrolysis of cellulose was conducted at 423 K in water and the glucose yield was 7%; the TRS yield was 30% which was similar to that using Amberlyst-15. But the TON number using the MNPs@SiO\textsubscript{2}–SO\textsubscript{3}H catalyst was much higher than that using Amberlyst-15 (3.8 vs. 0.4 (Table 6).

### 4.7 Supported metal catalysts

Supported metal catalysts have been widely used in biomass conversion due to their excellent hydrogenation activities. Numerous works have focused on the conversion of cellulose into sugar alcohols with supported metal catalysts in the presence of acids.\textsuperscript{113–115} Cellulose was hydrolyzed to sugars over acid and then hydrogenated into the sugar alcohols by supported metal catalysts under H\textsubscript{2} pressure. However, the hydrolysis of cellulose to glucose is rarely catalyzed solely by supported metal catalysts. Recently, Fukuoka et al.\textsuperscript{116} successfully converted cellulose to glucose by using a supported Ru catalyst. Various supported materials, including mesoporous carbon materials (CMKs), carbon black (XC-72), activated carbon (AC) and C\textsubscript{60} were tested and the CMK supported Ru catalyst (Ru/CMK-3) showed the best performance (the glucose yield was 34% and the oligosaccharide yield 5%). The loading amount of Ru on the catalyst had an apparent effect on the product distribution. When the Ru loading ranged from 2% to 10%, the glucose yield increased from 28% to 34% while the oligosaccharides decreased from 22% to 5%. The yield of total reducing sugars was ca. 40% regardless of the Ru loading. Besides, CMK-3 itself catalyzed the hydrolysis of cellulose in water at 503 K and gave a 21% yield of glucose and 22% yield of oligosaccharides (total 43%). The above results show that CMK-3 is able to convert cellulose into oligosaccharides and sugars, and Ru plays a very important role in the conversion of oligosaccharides into glucose. Further experiments on the hydrolysis of cellobiose with CMK-3 and Ru/CMK-3 confirmed the suspicion. The hydrolysis of cellobiose with Ru/CMK-3...
under the optimized conditions yielded 25% glucose, while the CMK-3 support gave a similar performance to the blank test (6.5% and 7.9% yield of glucose), which meant that the support had no activity in the hydrolysis and the Ru species played the role of hydrolyzing the β-1,4-glycosidic bonds (Scheme 12). Later work showed that the active Ru species was RuO$_2$·H$_2$O which was proposed to desorb the hydrated water to give a Lewis acid site that can depolymerize cellulose to glucose. Another hypothesis was that the Ru species worked as a Bronsted acid by the heterolysis of water molecules on Ru which had a low pK$_a$. The new method for the hydrolysis of cellulose without acids has a bright future for the development of new metal catalysts in the hydrolysis field.

4.8 Others

Recently, many new catalysts have emerged as powerful tools for the hydrolysis of cellulose to sugars. Zhang and Fang reported the effective use of ferrate CaFe$_2$O$_4$ as a heterogeneous catalyst for cellulose hydrolysis. In their work, an ionic liquid was used for pretreatment to reduce the crystallinity. The reaction was carried out at 423 K over 24 h. The best yield of glucose was achieved with fresh CaFe$_2$O$_4$ catalyst on hydrolyzing the pretreated cellulose; the glucose yield was 37% and the selectivity was 74%. The catalyst could be reused several times without much drop in the activity.

Hydrotalcite [Mg$_4$Al$_2$(OH)$_{12}$CO$_3$·4H$_2$O], activated by saturated Ca(OH)$_2$, was used as an inorganic catalyst for the hydrolysis of cellulose, as reported by Fang et al. The reaction was carried out at 423 K over 24 h with ball-milled cellulose; the conversion and glucose selectivity were 46.6% and 85.3%, respectively. The catalyst could be reused 4 times and the catalytic activity remained. Compared with carbon-based solid acids, the activated hydrotalcite catalyst is more stable and can be separated more easily from the reaction mixture.

5. Summary and outlook

The hydrolysis of cellulose to glucose is a critical step for the production of cellulosic bioethanol and many other value-added molecules. So far, the hydrolysis process cannot be amplified to industrial scale production due to its low economy and efficiency. The catalytic systems mentioned above were aimed at overcoming these limitations. Solid acids have many advantages over conventional liquid acids, in separation, recycling and being environmental benign. However, the mass transfer limitations between the insoluble polymers and heterogeneous catalysts are bottlenecks for the hydrolysis system. Conceptually, solid acids having higher specific surface areas, pore sizes/volume and strong acid sites are prone to exhibit better performances in the reaction. The number of Bronsted acid sites, affinity with the substrates and catalyst stability are all key factors in the hydrolysis reaction. Among the mentioned solid catalysts, carbon-based solid acids bearing –SO$_3$H, –COOH and –OH groups and cellulose-mimetic catalysts have strong affinity to the cellulose chain and make the acid sites closer to the β-1,4-glycosidic bonds. Magnetic solid acids are promising materials for the reaction due to their easier separation and recyclability. Heteropoly acids have been proven to be active catalysts for cellulose conversion, but their water solubility limits their large-scale application. Incorporation of HPAs into supports or the use of insoluble salts of HPAs may solve the problem and require further investigation.

Recent advances in the introduction of ionic liquids, microwave irradiation, supercritical water and nanoparticles to the cellulose hydrolysis system may allow the reaction to proceed more easily under milder conditions. Besides, cellulose pretreatment can reduce the degree of polymerization of cellulose and increase the surface area which would significantly improve the reaction efficiency and reduce the operation cost. All these technologies help to overcome the recalcitrance of cellulose and depolymerize it to a certain extent. Pretreatment is also the first step in the conversion of lignocellulosic biomass to chemicals, thus more convenient and efficient pretreatment methods, reaction media and advanced heating methods should be considered in the hydrolysis of cellulose.

Although cellulose hydrolysis has been developed with solid acids toward the greener synthesis of sugars, the reaction efficiency and selectivity still need to be improved. The development of highly acidic catalysts with nanometre size, good substrate affinity and thermal stability is a challenge towards practical systems. The production of fuels and chemicals from biomass requires multidisciplinary collaboration of researchers from enzymatic, homogeneous, and heterogeneous catalysis and the bio-/chemical engineering research areas. Economic, environmental, and sustainable aspects should all be considered when designing new catalytic systems.

We thank the 973 Program (2012CB215305, 2012CB215306), NSFC (21172209) and CAS (KJCX2-EW-J02) for financial support.

Notes and references


